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(54) Abstract Title

Method of making a collagen membrane

(57) A method of making an edible collagen membrane from porcine rinds for wrapping food products, said method comprising the steps of: freezing and thawing rind material, defatting rind material, acidic hydrolysis of rind material and grinding the resulting product into a gel-like mass. The gel is then extruded, sheeted and dried into a collagen membrane. A collagen membrane comprising an edible sheet containing primary collagen derived from porcine skin is also claimed.

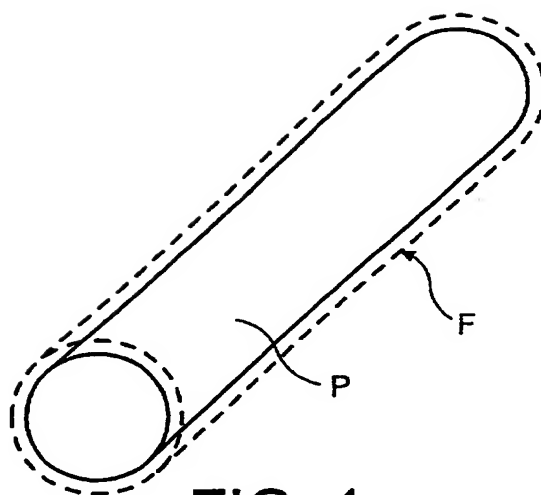


FIG. 1

METHOD OF MAKING A COLLAGEN MEMBRANE

5 The present invention relates generally to the making of collagen membranes and, more specifically, to the making of edible collagen membranes for wrapping food products, such as hams and the like.

10 Collagen membranes (a.k.a.: films, foils, etc.) are used in a variety of applications, such as illustrated in U.S. Patent Nos: 5,736,180 (Spice impregnated edible wrapping foil); 5,520,925 (Material on the basis of collagen fibres for covering wounds); 5,190,810 (Composite for use in making protective articles for use
15 in laser surgery); 5,103,816 (Composite for use in making protective articles for use in laser surgery); 5,028,695 (Process for the manufacture of collagen membranes used for haemostasis, the dressing of wounds and for implants); and 4,131,650 (Collagen foil for
20 cosmetic application).

 As illustrated in U.S. Patent No. 5,736,180, some edible collagen foils are known for, among other uses, wrapping food products, such as hams.

25 Collagen foils can be made from a variety of animal skins. However, making collagen foils from porcine skins (i.e. pig skins) presents a number of unique problems when compared to making such from, for example, cattle or bovine. For instance, problems result from the high fat content of porcine skins and the need to
30 remove the porcine hair.

 Currently, there are some procedures for preparing collagen foils from porcine skins, but these procedures are not satisfactory for the preparation of food products and the like from the collagen foil produced.
35 The existing procedures focus on the preparation of the porcine skins for the creation of "leather" goods that are processed at tanneries or the like.

Currently, collagen foils are prepared from porcine skins using the following steps:

5 (a) Porcine skins are collected from an abattoir (i.e. an establishment for slaughtering) and are usually preserved with sodium chloride and sold via skin traders to tanneries (i.e. establishments for converting skins into leather). At the tanneries, the goods are first washed with water and wetting agents and, if necessary, enzymes are also used to remove adhering faeces and sodium chloride. During additional steps, hair is removed from the skins using sodium sulfide and lime and, if necessary, using enzymes and lubricants. As a result, the skins (which are alkaline) are swollen to a thickness of approximately 5-10 mm.

15 (b) To further process the skins into leather, the skins are horizontally "split" into two layers. The lower layer, i.e. that which is directed toward the animals's body, serves as the starting material for the manufacture of collagen foils. Depending upon the tannery, as an intermediate step, the material is often stored for an indefinite period in unhygienic conditions.

25 (c) The "splits" are then subjected to a solution of caustic soda and/or lime in an alkaline hydrolysis process that can last for up to about 15 days. Through the hydrolysis process, the material becomes prepared for additional steps, particularly mincing. Due to the molecular characteristics of the bovine skin collagen used (reticular network), hydrolysis processes ranging from intense to aggressive are required. After the alkaline hydrolysis, the splits are subjected to a strong acid treatment, e.g. with hydrochloric acid, brought to a pH < 3.5, and then ground to a gel-like mass. Or, after alkaline treatment, the skins are brought to a pH of 5-7 using organic or inorganic acids, ground to a fibrous pulp, and then brought to a pH of < 3.5. The fluid pulp, which contains less than 2.5%

collagen, and to which other materials, such as glycerin, Karion® (sorbitol), and cross-linking agents have been added, is extruded and dried in a band dryer to the foil.

5 The above-described procedures have significant disadvantages. In particular, the present inventors have found that the foregoing procedures are not satisfactory for the preparation of foodstuffs and the like. The present inventors have noted that the
10 foregoing procedures have, for example, the following particular disadvantages:

- The preserving salts may contain additives that should not appear in food.

15 - The skins are not cleaned and are stored with faecal contamination.

- The goods can be of questionable origin (i.e. in the trade of skins, there are also goods of questionable origin, such as, e.g., skins from knackeries).

20 - The processing in the tannery is based on the requirements for leather production using technical chemicals.

- The product is transported in a non-refrigerated state to the foil manufacturers. As a
25 result, in the warmer seasons, there is the potential for increased bacterial contamination. This contamination can even be substantial enough to cause partial putrefaction of the material. The alkaline product can also potentially undergo uncontrolled
30 chemical decomposition, depending on the temperature and the time interval between the splitting and the delivery to the foil manufacturers.

- The quality of the raw material for the foils is subject to extreme deviations due to the complex
35 series of steps to which this is subjected.

- The aggressive alkaline treatment (hydrolysatation) also leads to denaturing alterations in

the collagen.

The present invention seeks to address the above-noted and other problems in the making of collagen membranes, especially in the making of edible collagen membranes from porcine skins (a.k.a.: pig skins or pork rinds).

According to a first aspect the invention provides a method of making a collagen membrane (which may also be referred to as collagen foil, film, etc.), said method comprising the steps of:

- a) defatting a porcine rind material;
- b) chemically dehairing the rind material;
- c) performing an acidic hydrolysis on the rind material;
- d) grinding the rind material; and
- e) extruding, sheeting and drying a resulting gel-like mass whereby to form a collagen membrane.

Preferably, the invention provides a method of making a collagen membrane from porcine rind material, said method comprising the steps of

- a) defatting the rind material to remove a majority of fat from the rind material;
- b) chemically dehairing the rind material;
- c) performing an acidic hydrolysis on the rind material;
- d) reducing the rind material into a gel-like mass of rind material; and
- e) extruding, sheeting and drying the gel-like mass into a collagen membrane.

Particularly preferably, the method of the invention comprises the steps of: removing skins from a porcine and promptly freezing the removed skins for processing; enzymatically defatting the rinds; performing a rapid alkaline hydrolysis on the rinds; performing an acidic hydrolysis on the rinds; grinding the rinds into a gel-like fluid mass; and extruding, sheeting and drying the gel-like mass whereby

to produce a collagen membrane.

According to another aspect the invention provides a collagen membrane made by the method herein described. In one preferred embodiment, the collagen membrane is
5 wrapped around a food product, such as a ham.

The above and other aspects, features and advantages of the invention will be further understood based on the following description of the preferred embodiments in combination with the accompanying figure,
10 in which:

FIG. 1 is a schematic diagram showing a finished collagen foil on a product, such as a ham or other meat product.

The method of the invention preferably includes the
15 following general method steps (sequence of the steps may be altered):

- (a) collecting/freezing of the rinds
- (b) defatting
- (c) dehairing/alkaline treatment
- 20 (d) acid treatment
- (e) forming into a gel-like mass
- (f) extruding/drying

In step (a), immediately after removing the porcine rinds at the abattoir (i.e. promptly upon removing (e.g.
25 skinning) the rinds from the hogs at the abattoir's establishment), the rinds are washed with cold or hot water and dehaired. After this the rinds are promptly frozen for use as a starting material for the production of the collagen membrane. Preferably, the rinds are
30 quickly frozen while in a very clean condition and, thus, preserved for use. A variety of freezing techniques can be employed, such as, for example, subjecting the rinds to a -50°C quick freezer or to a normal freezer at -18 to -28°C. It is also possible to
35 subject the rinds to dry ice or liquid nitrogen. It is also possible to start the process directly with fresh, unfrozen rinds.

Preferably, the rinds are maintained in such a frozen state until the rinds are subsequently processed as discussed below. In this regard, the subsequent processing steps are typically conducted at a different location than the establishment of the abattoir and, thus, the rinds are also preferably transported in this frozen state. For the subsequent processing, step (b) et seq, discussed below, the frozen rinds should preferably be thawed out to facilitate such processing.

10 In step (b) the rinds are defatted in one or more steps. This defatting is preferably carried out enzymatically with the help of wetting agents (e.g. detergents). Before starting the chemical process, it is also possible to defat the rinds mechanically
15 (removing fat over 15% of initial fat content). Also, defatting with water and surfactant or with organic solvents is possible.

In step (c) alkaline treatment is performed with alkaline organic or inorganic agents. This treatment
20 may be combined with the removal of the porcine bristles. Strong alkaline reagents such as sodium hydroxide or potassium hydroxide are able to dissolve the bristles and soften the collagen fibre structure. Also inorganic or organic reducing agents like sulfides
25 (e.g. sodium sulfide, potassium sulfide) or thio compounds (e.g. thioalcohols, thiourea, thioglycol) are able to dissolve the bristles.

In step (d), the rinds are brought to a maximum pH of 4.0 with acidic agents such as inorganic (e.g.
30 hydrochloric acid, sulfuric acid, phosphoric acid) or organic acids (e.g. lactic acid, citric acid, formic acid, acetic acid). During this treatment the rinds take up water (i.e. swell). This is important for the transformation of the rinds into a gel-like mass.
35 Alternatively, it is possible to neutralize the rinds with acidic agents to a pH of 4-8, most preferably pH 5-7. The resulting deswollen material can then be

milled into a fibre slurry. Later this slurry is acidified to $\text{pH} < 4$ to obtain the gel-like mass.

5 In step (e) the swollen rinds are ground into a gel-like mass. Alternatively, it is possible to grind unswollen rinds at $\text{pH} > 4.0$ into a collagen slurry and perform the acidification to produce the gel-like mass in a subsequent processing.

10 In step (f) the fluid mass is subjected to known extrusion and drying steps that are analogous to those of prior art procedures utilized with bovine skins, as discussed herein.

The method of the present invention has substantial advantages over the existing procedures. Some exemplary advantages include that:

15 (i) Step (a) of the present method can advantageously

- Provide a product that is appropriate for foodstuffs;

20 - Provide a starting material for the films that is of a consistently high quality;

- Avoid raw material from non-foodstuff sources;

- Avoid burdening or contamination of the raw material with chemicals;

25 - Avoid burdening or contamination of the raw material with microbiological contaminants;

- Avoid uncontrolled chemical decomposition of the raw material; and

- Avoid uncontrolled microbiological decomposition of the raw material.

30 (ii) In step (b) through (e), both the high fat content as well as the comparatively non-aggressive alkaline treatment can also prevent denaturing alterations in the collagen. Also moderate temperatures and non-aggressive bleaching steps essentially maintain
35 the collagen in its native state. With such a resulting collagen material it is possible to reduce or to avoid cross-linking agents in the final product. In contrast,

degraded collagen requires the use of cross-linking agents to get the desired tensile strength.

As discussed herein, the product (i.e. the collagen foil) produced by the process of the present invention
5 has a number of substantial advantages over existing collagen foils produced by the existing procedures. These advantages can include, for example, that:

- From the time of slaughtering, the microorganism count can be minimized, and there can be
10 substantially no increase in the microorganism count. The present foil can be made free of pyrogens and other metabolic products of microorganisms.

- The new foil can display a higher natural fat content. The foil can, thus, be less absorbent for
15 water and also more elastic. The foil can, thus, require less -- or even no -- chemical emollients. In addition, the reduced water absorbency can improve the foil's malleability.

- The product of the present invention can also
20 have a better native structure. The foil can be more elastic as well as more stable, and needs only minimal treatment -- or even no treatment -- with chemical cross-linking agents.

- The present product (due to the gentler
25 manufacturing process) can have a higher isoelectric point, which reduces the aqueous uptake in the neutral range. The foil, thus, remains more stable and is more malleable.

As described herein, the present product has
30 substantial benefits in applications where the collagen foil is used with foodstuffs or where the requirements for such collagen foil are similar to that of edible foils (e.g. where reduced contamination is desired). In a preferred embodiment, as shown in FIG. 1, the present
35 foil F is used in a method of wrapping a food product P. Most preferably, the present product is used in methods of wrapping meats and similar food products. In a

particularly preferred embodiment, the foil is used to wrap "hams". As noted below, it should be understood by those in the art that the present invention has a variety of benefits and uses that are applicable to a wide range of applications.

Normally the collagen film leaves the dryer very brittle (because of the very low water content). The fresh collagen film is difficult to handle. This very dry film shows a high affinity to water. The uptake of water and humidity is fast and difficult to control. For the customer, the quickly water-absorbing collagen film is difficult to control. Collagen film not immediately used takes up a high amount of water in humid air. A sticky foil can be the result, which is very difficult to handle in the machines. After some days, microbiological growth on the foil also can be a problem.

The incorporated residual natural fat makes the present product stable against any variation in humidity. The collagen foil leaves the dryer with preferably 11-13% residual water content. Even under humid air conditions this water content is stable and increases at most to a stable maximum of about 15%.

The porcine collagen fibres are much thinner than the bovine fibres. The resulting porcine foil is a much more compact woven material. This positively influences some important properties in its use as a wrap, e.g. oxygen permeability and humidity permeability. Normal oxygen permeability is about 1000-2000 ml/m² d bar, whereas that of the product of the invention is in the range of 200-500 ml/m² d bar. The normal humidity permeability is also about 1000-2000 g/m² d bar, whereas that of the product of the present invention is in the range of 100-300 g/m² d bar. Non-smoked products produced in accordance with the invention are better protected against chemical oxidation and loss of water.

The present invention can be utilized for wrapping

hams where a collagen film is transformed into a tube and the ham is placed inside the tube. Thereafter a net is wrapped around the ham. The product of the invention acts as a barrier membrane to reduce the loss of water of cooked ham and roast and also allows easy removal of the net.

The collagen product herein described can be utilized for the production of smoked ham, cooked salted meat articles, roast, scalded sausage, other sausages, fish products and pastry. The barrier membrane of the invention protects against water loss, loss of fat, etc.

The invention will now be described by way of the following non-limiting Examples.

In these exemplary embodiments, the treatment of the porcine skins after the above noted step (a) can include the specific procedural steps described below. (In the following description, the percentages are in relation to the weight of the rinds (i.e. the weight of the rinds = 100%) and the "mixer" used was a stainless steel reaction vessel.)

EXAMPLE 1

Step 1: (Defatting)

In a first step (following collection and freezing), the very fatty rinds are defatted. This defatting step is preferably carried out enzymatically with the help of wetting agents (e.g. detergents). Preferably lipases are used to hydrolyse natural fat between the collagen fibres. In addition, proteases are preferably used to support this action (i.e. to provide a more uniform defatting). In addition, a surfactant is preferably used to emulsify the released fatty acids. The combination of chemical and biochemical agents in this first step, and the advantages therefrom, were not previously contemplated in the field of preparing edible foils or films.

In a specific non-limiting example, this defatting can be carried out as follows (i.e. it should be understood that this is an exemplary embodiment and can be varied by those in the art depending on circumstances as appropriate (most preferable values in parenthesis):

Temperature: 10-35°C (30°C)

pH 7-11 (9-10)

(i) Place the following into the mixer

10	Rinds	100%	
	Water	50-150%	(100%)
	Sodium carbonate	0-5%	(3%)
	Fat dissolving enzymes	0-2%	(0.6%)
	(lipases)		
15	Protein dissolving enzymes	0-2%	(0.5%)
	(proteases)		
	(ii) Treatment in the mixer:	30min-3h	(1 hour)
	(iii) Add to the above in the mixer		
	Surfactant	0.05-3%	(0.5%)
20	(iv) Treatment time in the mixer:	30min-5h	(2 hours)
	(v) Rinse:		

Drain the water and dissolved chemicals from the mixer (e.g., via a drain).

25 **Step II: (Alkaline Treatment/Dehairing (i.e. the removal of the porcine bristles)**

In a second step, hair (e.g. roots within the skin) is removed from the porcine rinds. The presence of this hair is a problem particular to porcine skins. In this "hair-removal" step, a combination of chemicals, which preferably includes sodium sulfide, is used to dissolve this undesired hair or bristle material. This step and the advantages therefrom are also unknown in the field of edible foils. Normally dehairing of bovine skin takes place in tanneries under technical conditions. The use of sulfide in the dehairing of porcine rinds under foodstuff conditions is novel.

In a specific non-limiting example, this dehairing can be carried out as follows (most preferable values in parenthesis):

- 5 Temperature: 10-35°C (30°C)
pH > 9 (>12)
(i) Place in mixer:
- | | | | |
|----|----------------|--------|-------|
| | Lime | 0.5-5% | (3%) |
| | Water | 20-50% | (30%) |
| 10 | Sodium sulfide | 2-6% | (4%) |
- (ii) Treatment time in mixer: 2-8h (5.5 hours)
(iii) Add in mixer:
- | | | | |
|--|-------|--------------|-------|
| | Water | rest to 100% | (70%) |
|--|-------|--------------|-------|
- (iv) Treatment time in mixer: 5-30 min (10 mins)
15 (v) Rinse:

Drain the water and dissolved chemicals from the mixer.

Alternatively, sodium sulfide or other inorganic or organic reducing agents like potassium sulfide or thio compounds, e.g. thioalcohols, thiourea, thioglycol are able to dissolve the bristles. The lime/reducing agent could also be replaced by strong alkali e.g., sodium hydroxide or potassium hydroxide alone, to remove the bristles.

25

Step III: (Washing)

Then, the porcine skins are preferably subjected to a washing step. In a specific non-limiting example, the washing step can be carried out as follows (most preferable values in parenthesis):

- 30 Temperature: 10-35°C (30°C)
(i) Place in mixer:
- | | | | |
|--|-------|---------|--------|
| | Water | 50-200% | (100%) |
|--|-------|---------|--------|
- (ii) Treatment time in mixer: 5-30 min (10 mins)
35 (iii) Rinse:

Drain the water and dissolved chemicals from the

mixer.

Step IV: (Cleaning and Opening Up)

5 In a subsequent preferred step, the rinds are cleaned, preferably with peroxide to bleach the rinds. Preferably, sodium hydroxide is used so as to provide an alkaline condition which enhances peroxide action.

10 The sodium hydroxide also "opens-up" the collagen structure - i.e. provides the first step of collagen fibre-separation. While sodium hydroxide is used in prior art collagen processing, "opening-up" of bovine rinds requires higher concentrations of sodium hydroxide used for much longer time periods than with porcine rinds. The collagen of bovine rinds is more cross-linked, and the material is harder and needs a stronger hydrolysis to "open-up" than does porcine rinds. For example, porcine rinds as used in the present invention can be processed with 0.3 - 0.8% sodium hydroxide for 1-2 hours. Bovine rinds need 1 - 1.5% sodium hydroxide for 12-24 hours or a lime suspension for at least 15 days.

20 In a specific non-limiting example, this step can be carried out as follows (most preferable values in parenthesis):

25

Temperature: 10-35°C (30°C)

pH 8-13 (9-11)

(i) Place in mixer:

30	Water	50-200%	(100%)
	Hydrogen peroxide (33-35%)	0-2%	(1%)
	Sodium hydroxide	0.3-0.8%	(0.6%)
	(ii) Treatment time in mixer:	1-2h	(1 hour)
	(iii) Rinse:		

35 Drain the water and dissolved chemicals from the mixer.

Step V: (Further Washing)

The porcine skins are preferably then subjected to a further washing step. In a specific non-limiting example, the further washing step can be carried out as follows (most preferable values in parenthesis):

Temperature: 10-35°C (30°C)

(i) Place in mixer:

	Water	50-200% (100%)
10	(ii) Treatment time in mixer:	5-40 min (20 mins)
	(iii) Rinse:	

Drain the water and dissolved chemicals from the mixer.

15 **Step VI: (Acidification)**

Following the above-described alkaline treatment and preferably at this point, a short acid treatment is conducted. In this step, additional opening-up is effected - specifically, hydrolysis of acid unstable cross-links takes place, dissolving acid soluble non-collagenous material in the rinds.

In a specific non-limiting example, the acidification can be carried out as follows (most preferable values in parenthesis):

Temperature: 10-35°C (30°C)

pH max. 3.5

(i) Place in mixer:

	Water	30-150% (70%)
30	Hydrochloric acid (31-33%)	2.5-10% (7%)
	(iii) Treatment time in mixer:	15 min-5h (2 hrs)
	(iv) Rinse:	

Drain the water and dissolved chemicals from the mixer.

35 Other possible acids: sulfuric acid, phosphoric acid or organic acids, e.g. lactic acid, citric acid, formic acid, acetic acid. Time for this step: 15

minutes to 5 hours.

Step VII: (Additional Washing)

5 The porcine skins are then preferably subjected to an additional washing step. In a specific non-limiting example, this washing step can be carried out as follows (most preferable values in parenthesis):

Temperature: 30°C

10 (i) Place in mixer:

Water 50-200% (100%)

(ii) Treatment time in mixer: 5-40 min (20 mins)

(iii) Rinse:

15 Drain the water and dissolved chemicals from the mixer.

(iv) Repeat steps (i) to (iii) until a pH of about 1.8-3.9 is achieved. In this manner, by increasing the pH, the collagen takes up water. Thus, the "water filled" material can be ground as follows directly into a gel-like mass.

20 After this step, the washed rinds preferably have a pH of about 2.5 and a collagen content of about 13-21%.

Alternatively, neutralization can be carried out instead of acidification. The material is ground into a collagen slurry which is then acidified into a gel-like mass (see Example 2).

Step VIII: (Grinding)

30 The washed rinds are preferably ground into a uniform gel-like mass. While grinding of skins to a gel-like mass is previously known in collagen processing, for improved grinding, the size is preferably reduced in at least three stages. In this manner, the collagen fibre can be much better protected than in comparison to the same size reduction using only, e.g. two stages. Notably, only the small collagen particle masses don't separate by the addition of water.

In a specific non-limiting example, the grinding step can be carried out as follows:

- 5 1. Dividing the rinds into approximately cubic centimetre pieces by mincing through plates with 10 mm holes or by chopping with blades.
2. Then, dividing the pieces into small pieces of approximately a few millimetre in diameter by mincing or pressing the material through a plate with 4 mm holes.
- 10 3. Then, grinding to < 1mm by pressing through < 1mm hole plates or with the aid of a colloid mill or with the aid of a homogenizer.

During these procedures additional water or ice may be added.

15 **Step IX: (Preparation of the Fluid Mass)**

In a further step, the mass is preferably mixed with water and softener. A portion of the water may be ice.

20 The softener includes for example dialcohols, trialcohols, polyalcohols, (e.g., glycerol) or polymer sugars (e.g., Sorbitol and Karion).

The collagen preparation procedure is very protective for the collagen. Therefore and importantly, 25 the collagen membrane produced in accordance with the invention normally needs no cross-linking agents for stabilization and improvement of mechanical properties.

However, if desired, the following chemicals could act as cross-linkers: Organic cross-linkers, e.g. di- 30 aldehydes, α -hydroxyaldehydes, di-isocyanates, bisacrylamides, acrolein, carbodiimides, anhydrides, diene, polyene; and inorganic cross-linkers, e.g. aluminum compounds. For application in the mass, water soluble and slowly reactive compounds (e.g. dialdehydes, 35 α -hydroxyaldehydes) are preferred. The water insoluble rapidly reactive compounds should only be applied to the dry foil.

In one exemplary non-limiting case, the values of the fluid mass can be about (most preferable values in parenthesis):

5	Collagen content:	1-25%	(1.8%)
	Glycerol:	0-1%	(0.5%)
	Sorbitol	0-1%	(0.2%)
	pH:	2-3.6	(2.5%)
	Temperature:	3-18°C	(8°C).

10 With respect to softening, it is noted that pure and dry collagen films are brittle. The step of softening creates collagen fibre separation to allow, e.g. fibres to easily change their positions with
15 adjacent fibres. In this regard, water is the preferred softener for collagen. The above mentioned softeners act indirectly -- that is, they are very hygroscopic and keep water in the collagen. However, these carbohydrates also have a significant disadvantage --
20 that is, they support microbiological growth because they are a good available carbon source.

While fats are direct and good softeners, covering the dry collagen foil with fats is not very effective. When that is done, the fats are incorporated only
25 between the fibres and not inside the fibres. Adding fat-emulsions into the collagen mass achieves better results, but this also has two disadvantages:

- 1) emulsifying agents are present in the collagen foil; and
- 30 2) the fat can migrate to the surface of the collagen foil because it is not fixed properly.

In preferred embodiments, non-removed natural fat is the best softener. This fat is well incorporated
35 between and inside the fibres. Preferably, in the present method, the chemical process is adapted such that it does not remove all of the fat. The remaining

fat, thus, is used as a softener and only a small amount -- or even no -- additional carbohydrate softener is needed. In comparison to other processes, the present invention is thus advantageous in working with fatty porcine rinds.

The removal of fat in the defatting step(s) depends on:

temperature
pH
time
amount of lipase
amount of surfactant
number of defatting steps
position in the process

Defatting is preferably carried out at a higher temperature (about 30°C), at pH 9-10, over extended time periods (up to e.g. 6 hours), with increased amounts of lipase (up to 1%), increased amounts of surfactant (up to 3%), more defatting steps (up to 5 or more over the whole procedure) and later in the process, e.g. after the alkaline treatment. The content of non-removed fat can be in the range of 0-10%, (dry weight of the foil).

With respect to cross-linking agents, it is noted that only natural unaffected collagen (i.e. that which substantially retains its original native structure) shows the best mechanical properties. With prior art procedures, high amounts of cross-linking agents are necessary after the normally strong alkaline processes in the chemical treatment (i.e., the hydrolysis of the collagen molecules). The cross-linking agents are used to synthetically reconstruct bigger molecules. With the present method, the collagen molecules can be protected and the amount of cross-linking agents can be kept to a minimum.

Step XII: (Homogenization)

After the foregoing, a homogenization step is

preferably performed. First, air bubbles are removed, then the slurry is passed to a homogenizer, and then the material is pumped into stainless steel vessels.

5 A chemical importance of homogenization is that it facilitates the uniform distribution of the water. Homogenization is the final step of reducing the size of collagen particles: fibre bundles and bigger particles are divided into fibres and fibrils. Preferably, the homogenization fulfills at least one, most preferably
10 all, of the following:

- 1) it does not affecting the fibre/fibril length;
- 2) it maximizes disintegration of fibre bundles into fibres/fibrils; and/or
- 3) it has a suitable fibres/fibrils relationship.

15 The above three points directly and strongly influence the mechanical properties of the collagen foil.

While disintegration steps are well known in collagen processing, the present method has not
20 previously been contemplated by those in the art. The present invention can utilize a conventional homogenizer or a colloid mill. The homogenization step can be carried out with the same machines as the grinding step described above. However, in homogenization, the mass
25 of material being homogenized has the final composition (water content, collagen content, softener content, pH, temperature), whereas the above-described grinding step is before final adjustment of these parameters. Thus, during the homogenization step, the material is ground
30 to less than 1mm, for example by pressing through plates having holes less than 1mm therein, or with the aide of a colloid mill or homogenizer.

Step XIII: (Extrusion, Sheetting And Drying)

35 Then, the slurry preferably undergoes the steps of extrusion, sheetting and drying. In this regard, the slurry is preferably first directed through a slit

extruder. The extruded slurry passing through the extruder is received on a conveyor belt. The slurry is preferably sheeted (e.g. with a sheeting roller). The extruded slurry is also preferably neutralized (e.g. directly after extrusion). Neutralization is preferably performed with ammonia gas, or with sodium hydrogencarbonate, or with other neutralization agents. It is noted that prior to entering the extruder, the slurry has a pH of about 2.0 - 3.6. At that pH level, the collagen particles are swollen (i.e. they have a high water content). This high water content typically leads to a deformation of the collagen on every level (e.g. molecules, microfibrils, elementary fibres, fibres). A direct drying of the slurry without neutralization can lead to a fixation of these deformations, such that the interaction of the collagen molecules is limited and the foil strength is weakened. Thus, as per the foregoing, after extrusion and before drying, a fibre formation step is preferably performed. This fibre formation step can involve neutralization to higher pH values, as per the above, or a coagulation with high ionic strength solutions.

The chemicals used for this fibre formation and the time permitted for fibre formation can influence the properties of the collagen foil. Ammonia gas, noted above, acts very quickly and, thus, may have some disadvantages in good fibre formation. Sodium hydrogencarbonate, also noted above, acts slowly, and, in consequence, the fibre formation and the mechanical properties of the collagen foil can be improved. Prior to the present invention, it was not previously contemplated to use of sodium hydrogencarbonate in this context in collagen processing.

The conveyor belt then preferably passes through a dryer. In the dryer, the neutralized slurry is preferably continuously air dried on the belt at about 60 - 90°C. The length of the dryer can be, as just one

non-limiting example, about 50 metres. The conveyor speed (e.g. the production speed) should be made to correspond to the length of the dryer. In one non-limiting example, when the length of the dryer is about 50 metres, the conveyor speed (e.g. directly related to the output of the collagen foil) can be about 3 - 9 metres per minute. Preferably, the cross-wise width of the foil on the conveyor is up to about 60 cm (but, this size can be varied depending on circumstances).

10 The present invention for producing collagen film from porcine rinds differs substantially from the prior art, which utilizes dehaired bovine splits having a very low fat content, collected from tanneries. Thus, the problems which the present invention seeks to address, i.e. defatting of the very fatty material and removing of the bristles, are unknown in the prior art field of collagen film production. The present collagen process protects the collagen, therefore it is possible to produce the collagen film without cross-linking agents. 20 The strong process used for bovine splits weakens the material, such that it is then necessary to stabilize the foil with cross-linking agents. To use no cross-linker is unknown in this art. Both the affected bovine collagen and the cross-linking leads to a collagen film with poor stretchability. On the other hand, high stretchability is an important quality criteria. Fat can improve the stretchability. For example, DE 196 40 019 A1 describes the addition of fat into a mass to get a more stretchable collagen film. With the 30 present invention, porcine fat in the porcine rinds leads to a collagen foil with very good stretching properties.

Step XIV: (Storage)

35 Then, a final storage, e.g. packaging, step is performed. Prior to packaging, the collagen foil is preferably air-conditioned (dried). Before packaging,

the humidity (moisture content) of the collagen film should be within the range of about 5-25%, more preferably about 10-20%, and most preferably between about 11 - 18% (the humidity level is related, for example, to the softening step and to the present air-conditioning step). Among other things, this preferred humidity range helps provide collagen foils that are better in use. In this regard, humidity levels below about 15% can make the collagen films too brittle, while humidity levels above about 20% can support excess microbiological growth. The product may have a thickness in the range of about 0.01-2mm, and a dry weight per square metre of about 10-50 g/m².

EXAMPLE 2

Step I: (Pretreatment)

In a first step the rinds are washed with a surfactant.

In a specific non-limiting example, this pretreatment can be carried out as follows (i.e. it should be understood that this is an exemplary embodiment and can be varied by those in the art depending on circumstances as appropriate (most preferable values in parenthesis):

Temperature: 10-25°C (20°C)

(i) Place the following into the mixer

Rinds	100%	
Water	50-200%	(100%)
Surfactant	0.2-3%	(1%)
(ii) Treatment time in the mixer:	30 min.-4h	(1 hour)
(iii) Rinse:		

Drain the water and dissolved chemicals from the mixer.

Step II: (Alkaline Treatment/Dehairing (i.e. the removal of the porcine bristles))

In a second step, hair (e.g. roots within the skin) is removed from the porcine rinds. The presence of this hair is a problem particular to porcine skins. In this "hair-removal" step, a combination of chemicals, which preferably includes sodium sulfide, is used to dissolve undesired hair or bristle materials. This step and the advantages therefrom are unknown in the prior art field of edible foils. Normally this dehairing step of bovine skins take place in tanneries under technical conditions. As noted above, the sulfide dehairing of porcine rinds under foodstuff conditions is considered novel.

In a specific non-limiting example, this dehairing can be carried out as follows (most preferable values in parenthesis):

Temperature: 10-25°C (20°C)

pH >9 (>12)

(i) Place in mixer:

Lime	0.5-5%	(3%)
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Water	20-50%	(30%)
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Sodium sulfide	2-6%	(4%)
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(ii) Treatment time in mixer:	2-8h	(5 hours)
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(iii) Add in mixer:

Water	rest to 100%	(70%)
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(iv) Treatment time in mixer:	5-30 min	(10 mins)
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(v) Rinse:

Drain the water and dissolved chemicals from the mixer.

Step III: (Washing)

Then, the porcine skins are preferably subjected to a washing step. In a specific non-limiting example, the washing step can be carried out as follows (most preferable values in parenthesis):

Temperature: 10-35°C (30°C)

(i) Place in mixer:

Water

50-200% (100%)

(ii) Treatment time in mixer:

5-30 min (10 mins)

5 (iii) Rinse:

Drain the water and dissolve chemical from the mixer.

Step IV: (Defatting)

10 In this defatting step the rinds are defatted.
This defatting step is preferably carried out
enzymatically with the help of wetting agents (e.g.
detergents). Preferably lipases are used to hydrolyse
natural fat between the collagen fibres. In addition,
15 proteases are preferably used to support this action
(i.e. to provide a more uniform defatting). In
addition, a surfactant is preferably used to emulsify
the released fatty acids. This first step, including
the combination of chemicals and biochemical agents
20 therein, and the advantages therefrom was not previously
contemplated in the field of preparing edible foils.

In a specific non-limiting example, this defatting
can be carried out as follows (i.e. it should be
understood that this is an exemplary embodiment and can
25 be varied by those in the art depending on circumstances
as appropriate). (Most preferable values in
parenthesis):

Temperature: 10-35°C (30°C)

30 pH 8-13 (9-11)

(i) Place the following into the mixer

Water

50-200% (100%)

Fat dissolving enzymes

0-2% (0.6%)

(lipases)

35 (ii) Treatment time in the mixer:

15 min.-6h (1 hour)

(iii) Add to the above in the mixer:

Protein dissolving enzymes

0-2% (0.5%)

(proteases)

Surfactant 0.05-3% (0.5%)

(iv) Treatment time in the mixer: 1-12h (4 hour)

(v) Rinse:

5 Drain the water and dissolved chemicals from the mixer.

Step V: (Further Washing)

10 Then, the porcine skins are preferably subjected to a further washing step. In a specific non-limiting example, the further washing step can be carried out as follows (most preferable values in parenthesis):

Temperature: 10-35°C (30°C)

15 (i) Place in mixer:

Water 50-200% (100%)

(ii) Treatment time in mixer: 5-40 min (20 mins)

(iii) Rinse:

20 Drain the water and dissolved chemicals from the mixer.

(iv) Place in mixer:

Water 50-200% (100%)

(v) Treatment time in mixer: 5-40 min (20 mins)

(vi) Rinse:

25 Drain the water and dissolved chemicals from the mixer.

Step VI: (Neutralization)

30 Then, following defatting, a neutralization step is conducted. In a specific non-limiting example, the acidification can be carried out as follows (most preferable values in parenthesis):

Temperature: 10-35°C (30°C)

35 pH max. 3.5

(i) Place in mixer:

Water 50-200% (100%)

citric acid 0.5-2% (1%)
(iii) Treatment time in mixer: 2-5h (3 hours)
(iv) Rinse:

5 Drain the water and dissolved chemicals from
the mixer.

(v) Place in mixer:

Water 50-200% (100%)
mono sodiumcitrate 0.5-5% (2%)

(vi) Treatment time in mixer: 2-5h (3 hours)

10 Adjusting the pH with hydrochloric acid (10%):

(vii) Add to the above in the mixer

hydrochloric acid (10%) 0.2-2% (1%)

(viii) Treatment time in mixer 30min.-5h (2hrs)

15 Repeat steps (vii) - (viii) until pH about 5 is
reached

(ix) Allow the mixer to stand overnight

(x) Rinse:

Drain the water and dissolved chemicals from the
mixer.

20

Step VII: (Additional Washing)

In a specific non-limiting example, the additional
washing step can be carried out as follows (most
preferable values in parenthesis):

25

Temperature: 10-35°C (30°C)

(i) Place in mixer:

Water 50-200% (100%)

(ii) Treatment time in mixer: 5-40 min. (20 mins)

30

(iii) Rinse:

Drain the water and dissolved chemicals from
the mixer.

The material is ground into a collagen slurry which
is then acidified into a gel-like mass.

35

Step VIII: (Grinding)

As in Example 1.

Step IX: (Milling)

The ground material is mixed with 5 parts water and 3 parts ice. Milling is effected in a colloid mill to produce a uniform collagen slurry.

5

Step X: (Mass preparation)

In a further step, the slurry is preferably mixed again with water, ice, hydrochloric acid and softener to produce a uniform gel-like mass.

10

In one exemplary non-limiting case, the resulting properties of the mixed mass can be about:

	Collagen content:	1-2.5%	(1.8%)
	Glycerol	0-1.2%	(0.6%)
	pH:	2-3.6	(2.8)
15	Temperature:	3-18°C	(8°C)

Claims:

1. A method of making a collagen membrane, said method comprising the steps of:
 - 5 a) defatting a porcine rind material;
 - b) chemically dehairing the rind material;
 - c) performing an acidic hydrolysis on the rind material;
 - d) grinding the rind material; and
 - 10 e) extruding, sheeting and drying a resulting gel-like mass whereby to form a collagen membrane.
- 15 2. The method of claim 1 wherein steps a) to e) are effected sequentially.
3. The method of claim 1 wherein step b) is effected prior to step a).
- 20 4. The method of claim 1 or claim 3 wherein step d) is effected prior to step c).
- 25 5. The method of any preceding claim, further including the step of removing skins from a porcine and freezing the removed skins to provide said porcine rind material.
6. The method of any preceding claim wherein the rind is enzymatically defatted.
- 30 7. The method of any preceding claim wherein said rind material is defatted whereby to produce a collagen membrane having a fat content of about 10% or less based on the dry weight of the collagen membrane.
- 35 8. The method of any preceding claim wherein said dehairing of the rind material comprises alkaline treatment of said rind material.

9. The method of any preceding claim wherein after the dehairing step, the rind material is washed.

5 10. The method of claim 9 wherein after the washing step, the rind material is treated with peroxide and sodium hydroxide.

10 11. The method of claim 10 wherein after the treatment with peroxide and sodium hydroxide, the rind material is subjected to a further washing step with water.

15 12. The method of any preceding claim wherein after the acidic hydrolysis of the rind material, the rind material is subjected to a washing step with water whereby to achieve a pH of about 1.8-3.9.

13. The method of any preceding wherein the rind material is reduced to a gel-like mass by grinding.

20 14. The method of any preceding claim wherein the gel-like mass is mixed with a softener prior to extruding, said softener being selected from the group consisting of dialcohols, trialcohols, polyalcohols and polymer sugars.

25 15. The method of claim 13 wherein, after grinding, the gel-like mass is homogenized.

30 16. The method of any preceding claim wherein the gel-like mass has a pH of about 2.4-3.6 prior to extruding.

17. A collagen membrane obtainable by the method of any preceding claim.

35 18. A collagen membrane comprising an edible sheet containing primary collagen derived from porcine skin.

19. An edible collagen membrane, said membrane being substantially free from non-native collagen and comprising a purified collagen material derived from porcine skin.

5

20. The collagen membrane of any one of claims 17 to 19 having a moisture content of from 5-25%, preferably from 11-18% by weight.

10

21. The collagen membrane of any one of claims 17 to 20, having a thickness in the range of about 0.01-2mm.

22. The collagen membrane of any one of claims 17 to 21, wrapped around a food product.

15

23. The collagen membrane of claim 21, wherein the food product is ham.

20

24. A food product comprising a collagen membrane as claimed in any one of claims 17 to 21.

25. Use of a collagen membrane as claimed in any one of claims 17 to 21 as a wrapping for a food product.

25

26. A method substantially as herein described with reference to any one of the Examples and/or Figure 1.

30

27. A collagen membrane substantially as herein described with reference to any one of the Examples and/or Figure 1.



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Application No: GB 0029916.4
Claims searched: 1-27

Examiner: Dr Jeremy Kaye
Date of search: 22 May 2001

Patents Act 1977 Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
UK CI (Ed.S): A2B (-BAFA, BMM2, BMX, BAFOX)
Int CI (Ed.7): A22C 13/00, 17/00, 17/12; A23L 1/31, 1/312.
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Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
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X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
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